

Breaking of scale-invariance symmetry in adsorption processes

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Abstract. – Standard models of sequential adsorption are implicitly formulated in a *scale invariant* form, by assuming adsorption on an infinite surface, with no characteristic length scales. In real situations, however, involving complex surfaces, intrinsic length scales may be relevant. We present an analytic model of continuous random sequential adsorption, in which the scale invariance symmetry is explicitly broken. The characteristic length is imposed by a set of scattered obstacles, previously adsorbed onto the surface. We show, by means of analytic solutions and numerical simulations, the profound effects of the symmetry breaking on both the jamming limit and the correlation function of the adsorbed layer.

The irreversible adsorption of colloidal particles onto a solid surface [1, 2] has been the subject of a particularly active research effort over the last years. The kinetics of adsorption has been mainly studied through the formulation of different models, aiming to capture the essential features of the process. These models are defined via a set of rules by which the particles accommodate when arriving at the surface, and their main purpose is to reproduce the experimentally observed properties of the adsorbed phase. Among those, we emphasize the maximum density of adsorbed particles—the *jamming limit* ρ_∞ —and the structure of the adsorbed layer, as measured by the correlation function $g(x)$ [2]. In the basic models proposed so far (the random sequential adsorption model (RSA) [3, 4, 5, 6, 7, 8], the ballistic model [9, 10, 11], and their subsequent extensions), the kinetics is considerably simplified, both numerically and analytically, by assuming that the adsorption takes place onto a *planar* surface of *infinite* extension. Under this condition, and given that there is no characteristic length involved in the problem (apart from the size of the particles) it is presumable that the basic dynamic quantities satisfy certain scaling laws. The existence of those scaling laws is ultimately responsible for the fact that, once the model is established by predicating a certain set of rules, all relevant quantities remain fixed and their values depend only on the rules adopted. In particular, all properties are independent of the particle size and the rate of adsorption—this latter assumed to be constant in space and time. Moreover, in the absence of external forces or interactions among the particles [12, 13, 14], the adsorbed layer exhibits

a simple structure in which correlations decay very fast, thus indicating absence of long range order. Although models formulated under those conditions may accurately reproduce many experimental situations, their extension to more complex surfaces having an intrinsic structure is by no means trivial. For example, a characteristic length may be present in the substrate, which may alter the kinetics of the process and the structure of the adsorbed layer. With the only exception of some discrete models formulated to analyze adsorption in the presence of point-like quenched impurities [15, 16], and a model of RSA of spherical particles adsorbing onto a substrate composed by a random collection of points [17], the physics on those complex substrates (beyond the scaling regime) remains essentially unexplored.

Our purpose in this Letter is to show that when the scale invariance is broken by introducing a characteristic length, new aspects of the problem arise, leading to considerable changes in the adsorbed layer. The appearance of new scales may originate from the existence of pinned objects on the surface [15, 16]. Thus, to make our analysis concrete, we will present an extensive study of a one-dimensional (1d) model in which particles adsorb according to the RSA rules onto a line where a distribution of spherical obstacles of different size has been previously dispersed. We note that this model is essentially different from those of Refs.[18, 19, 20, 21, 22], which deal with the *simultaneous* adsorption of particles of different sizes.

In the RSA model [2, 4], the adsorbing particles are sequentially located at random positions on the surface. If an incoming particle overlaps with a previously adsorbed one, it is rejected; otherwise, it becomes irreversibly adsorbed. The continuous version of this model can be solved in 1d by analyzing the density function of gaps—holes between two consecutively adsorbed particles. In the RSA of spheres of a single diameter σ , the density of gaps of length x , $G_\sigma(x, t)$, fulfills the equations [10]

$$\frac{\partial G_\sigma(x, t)}{\partial t} = -(x - \sigma)G_\sigma(x, t) + 2 \int_{x+\sigma}^{\infty} G_\sigma(y, t)dy, \quad x \geq \sigma; \quad (1)$$

$$\frac{\partial G_\sigma(x, t)}{\partial t} = 2 \int_{x+\sigma}^{\infty} G_\sigma(y, t)dy, \quad x \leq \sigma. \quad (2)$$

Here time t has been rescaled by the rate of arrival of the particles to the line and it has therefore units of inverse length. The subscript σ explicitly denotes the dependence on the size of the particles. The coverage $\rho_\sigma(t)$ is given by $1 - \int_0^\infty xG_\sigma(x, t)dx$. The solution of Eqs. (1) and (2), with the initial condition of an infinite clean substrate [i.e., $G_\sigma(x, 0) = 0$] yields the result $\rho_\sigma(t) = \psi(\sigma t)$ [10], where $\psi(t) \equiv \int_0^t F(u)du$ is the coverage corresponding to an RSA process with particles of size 1. We have defined the usual function $F(t) \equiv \exp\left\{-2 \int_0^t dz(1 - e^{-z})/z\right\}$.

From this solution we see that $\rho_\infty = \lim_{t \rightarrow \infty} \rho_\sigma(t) \equiv \rho_R = 0.74759$ [4], independent of σ . This fact can be understood by noticing that the gap distribution, as given by Eqs. (1) and (2), fulfills the identity

$$G_{\lambda\sigma}(x, t) \equiv \lambda^{-2}G_\sigma(\lambda^{-1}x, \lambda t), \quad (3)$$

for any real positive number λ . This identity means that the gap density G_σ is *scale invariant*: covering the line (and in general any surface) with particles which are larger by a factor λ has the only effect of reducing the time at which a given configuration is reached, by a factor of λ^{-1} . It is the existence of this scale invariance that is responsible for the fact that the jamming limit remains fixed upon variations of the particle size σ .

The presence of impurities—defined as preadsorbed obstacles of a fixed size $\sigma_0 \neq \sigma$ —breaks the scale invariance by introducing an external length scale. The jamming limit and

the structure of the adsorbed phase must therefore depend in this case on the size of the adsorbing particles, more precisely, on the size ratio of particles to obstacles, $r = \sigma/\sigma_0$.

We consider in general the adsorption of particles of size σ onto a linear substrate, over which there is a preadsorbed set of obstacles of size σ_0 , present with an initial density ρ_0 . Assuming that the impurities have been adsorbed onto the surface following the RSA dynamics, they reach the coverage ρ_0 at time t_0 ,

$$\rho_0 = \psi(\sigma_0 t_0) = \psi(\zeta_0). \quad (4)$$

The dependence of ρ_0 on t_0 is through the combination $\zeta_0 = \sigma_0 t_0$. At this time, the surface exhibits a gap distribution given by $G_{\sigma_0}(x, t_0)$. The problem translates then to solving Eqs. (1) and (2) with the initial condition that, at time t_0 , the gap density is given by $G_0(x) \equiv G_{\sigma_0}(x, t_0)$.

We contemplate two possibilities, namely $\sigma > \sigma_0$ and $\sigma < \sigma_0$. The instance $\sigma > \sigma_0$ has been previously considered in the literature, numerically [15, 16, 23] and analytically [16, 23, 24], on one- and two-dimensional lattice (discrete) models. In this case, the imposed characteristic length is small, thus implying slight variations of the form of the surface with respect to the planar form. The first characteristic we want to show is that our model admits in this case a very direct solutions, which agrees with the continuum limit of the lattice models previously proposed.

To show this, we perform in Eq. (1) the substitution $G(x, t) = e^{-(x-\sigma)t} H(t)$. The corresponding equation for $H(t)$ is then $dH/dt = (2e^{-x\sigma}/t)H$, which is solved with the initial condition $H(t_0) = H_0$. The constant H_0 is determined by comparison with the initial value $G_0^>(x) \equiv G_0(x > \sigma_0)$. We obtain

$$G(x, t) = \Upsilon_0 t^2 e^{-(x-\sigma)t} F(\sigma t), \quad x > \sigma, \quad (5)$$

where we have defined the constant

$$\Upsilon_0 = e^{-(\sigma-\sigma_0)t_0} \frac{F(\sigma_0 t_0)}{F(\sigma t_0)} \equiv e^{-(r-1)\zeta_0} \frac{F(\zeta_0)}{F(r\zeta_0)}. \quad (6)$$

Eq. (2) is solved by direct integration, yielding

$$G(x, t) = G_0(x) + \Upsilon_0 \int_{t_0}^t 2ue^{-xu} F(\sigma u) du, \quad x < \sigma, \quad (7)$$

where $G_0(x)$ equals $G_0^<(x) \equiv G_0(x < \sigma_0)$ or $G_0^>(x)$, according to the value of x . Further integration of the quantity xG , in the limit $t \rightarrow \infty$, yields the jamming limit

$$\rho_\infty = \rho_0 + \Upsilon_0 [\rho_R - \psi(r\zeta_0)]. \quad (8)$$

This result coincides with the continuum limit obtained from the lattice model in Ref. [23].

We turn now to the more complex case $\sigma < \sigma_0$, in which more interesting changes are expected, due to the fact that the planar form of the surface is considerably altered. The difficulty in solving the model stems from the coupling of the solution to the initial conditions. We consider in particular the case $\sigma_0/2 \leq \sigma \leq \sigma_0$; the case $\sigma < \sigma_0/2$ can be worked out along the same lines. The solution of the model is found for different ranges of values of x :

(a) $x > \sigma_0$: From Eqs. (2) and (5), we readily obtain

$$G^{(a)}(x, t) = \Upsilon_0 t^2 e^{-(x-\sigma)t} F(\sigma t). \quad (9)$$

(b) $\sigma_0 > x > \sigma$: From Eq. (1), we see that the equation is coupled to $G^{(a)}$. The solution is

$$G^{(b)}(x, t) = e^{-(x-\sigma)(t-t_0)} \int_0^{t_0} 2ue^{-ux} F(\sigma_0 u) du + \Upsilon_0 e^{-(x-\sigma)t} \int_{t_0}^t 2ue^{-\sigma u} F(\sigma u) du. \quad (10)$$

(c) $\sigma > x > \sigma_0 - \sigma$: Given $G^{(a)}$, the solution follows by direct integration:

$$G^{(c)}(x, t) = G_0^<(x) + \Upsilon_0 \int_{t_0}^t 2ue^{-xu} F(\sigma u) du. \quad (11)$$

(d) $\sigma_0 - \sigma > x > 0$: The equation for $G^{(d)}$ is coupled to the cases *a* and *b*. The solution is found to be

$$\begin{aligned} G^{(d)}(x, t) &= G_0^<(x) + 2 \int_{t_0}^t dv \int_0^{t_0} 2ue^{-\sigma u} \mathcal{L}_x(u+v-t_0) F(\sigma_0 u) du \\ &+ 2\Upsilon_0 \int_{t_0}^t dv \mathcal{L}_x(v) \int_{t_0}^v 2ue^{-\sigma u} F(\sigma u) du + \Upsilon_0 \int_{t_0}^t 2ue^{-(\sigma_0-\sigma)u} F(\sigma u) du, \end{aligned} \quad (12)$$

where we have used the auxiliary function

$$\mathcal{L}_x(z) = \frac{1}{z} \left\{ e^{-xz} - e^{-(\sigma_0-\sigma)z} \right\} \quad (13)$$

In order to estimate the covering at jamming, we compute the integral $\int_0^\infty xG(x, t)dx$. In the limit $t \rightarrow \infty$ the contribution from regions *a* and *b* vanishes, since at jamming there are no gaps of length larger than a particle diameter. After performing some cumbersome algebra, we arrive at the final expression for the total coverage, counting both particles and obstacles:

$$\begin{aligned} \rho_\infty &= \rho_0(1+r) + 2r \int_0^{\zeta_0} (e^{-ru} - 2e^{-u}) F(u) du \\ &+ 2r\Upsilon_0 \int_{\zeta_0}^\infty \left\{ [1 + (1-r)u] e^{-(1-r)u} + e^{-ru} - 2e^{-u} \right\} F(ru) du. \end{aligned} \quad (14)$$

Equation (14) determines the coverage at jamming for any value of $\rho_0 < \rho_R$, both explicitly and implicitly as a function of the initial time t_0 . We can however determine an explicit form as a function of ρ_0 in the limiting case $\zeta_0 \ll 1$ (small initial coverage ρ_0), by Taylor expanding the expression for $F(t)$. We obtain

$$\rho_\infty = \rho_R + (1-r)(1-\rho_R)\rho_0 + \mathcal{O}(\rho_0^3). \quad (15)$$

That is, up to corrections of order ρ_0^3 , ρ_∞ grows linearly with ρ_0 , with slope $(1-r)(1-\rho_R)$. Incidentally, we note that the same Taylor expansion is valid for the expression (8), corresponding to $\sigma > \sigma_0$. In this case, however, since $r > 1$, the jamming limit decreases linearly with ρ_0 .

For larger values of ρ_0 we can estimate the theoretical predictions of Eq. (14) by integrating this expression up to a very large time t . Given a value of ρ_0 , the corresponding time t_0 is found by numerically solving Eq. (4). Having obtained these two values, we perform the integration in Eq. (14). Figure 1 shows the results of such integration for different values of r , as a function of the initial density ρ_0 . The symbols represent data obtained from Monte Carlo simulations of the model on a line of length $L = 5000\sigma$ with periodic boundary conditions,

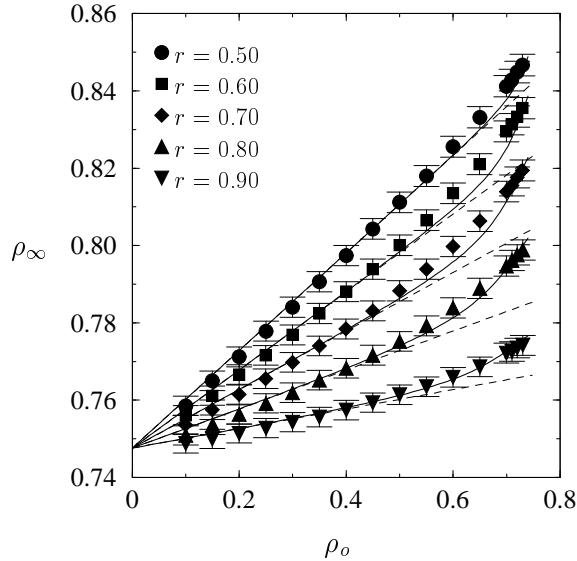


Fig. 1 – Jamming limit ρ_∞ as a function of the initial density ρ_0 . Full lines, analytic result Eq. (14); filled symbols, computer simulations; dashed lines, linear approximation Eq. (15).

averaging over 100 realizations. The error bars reported are standard deviations. The dashed lines correspond to the results obtained in the linear approximation (15).

From Figure 1 we observe that the jamming limit is very well approximated by the linear expression (15), up to a critical density $\rho_0^{(c)}$, above which ρ_∞ overshoots and increases faster. The critical density can be seen to depend approximately linearly on the size ratio, being a decreasing function of r . The presence of this critical density can be understood as follows: The effect of a small concentration of obstacles is to essentially impose a small perturbation in the structure of the adsorbed phase. For $r \ll 1$ and $\rho_0 \ll 1$, one can consider the interactions of particles and impurities as effectively decoupled. We are then in a situation where the particles saturate the surface up to a density ρ_R , leaving free a fraction $1 - \rho_R$ which is filled with impurities with density ρ_0 . This amounts effectively to a total coverage $\rho_\infty \approx \rho_R + (1 - \rho_R)\rho_0$, which indeed coincides with the exact Taylor expansion, Eq. (15), in the limit $r \rightarrow 0$. We can thus interpret this case as a *soft* symmetry breaking, which induces at most linear corrections to the jamming limit. When the density ρ_0 increases, the interaction between particles and impurities grows larger. Beyond $\rho_0^{(c)}$, the presence of impurities radically alters the structure of the adsorbed phase, breaking completely the scale invariance symmetry, and inducing non-linear corrections to the jamming limit.

We can assess the effects of the symmetry breaking on the structure of the adsorbed phase by studying the particle-particle correlation function $g(x)$. In Figure 2 we have plotted $g(x)$ as a function of the reduced length x/σ , for different values of ρ_0 and a fixed size ratio $r = 0.70$. Data is obtained from simulations onto a line of length $L = 10000\sigma$, averaging over 10 different realizations. The bin width used is $1/100$. For this particular value of r , we can estimate from Fig. 1 $\rho_0^{(c)} \approx 0.50$. For values of $\rho_0 < 0.50$, we observe that the correlation function has essentially the same shape as in standard RSA. At $\rho_0 = 0.50$, however, we observe the development of a secondary peak in $g(x)$, which eventually grows and takes over for larger concentrations. This peak corresponds to a majority of pairs of particles separated by exactly

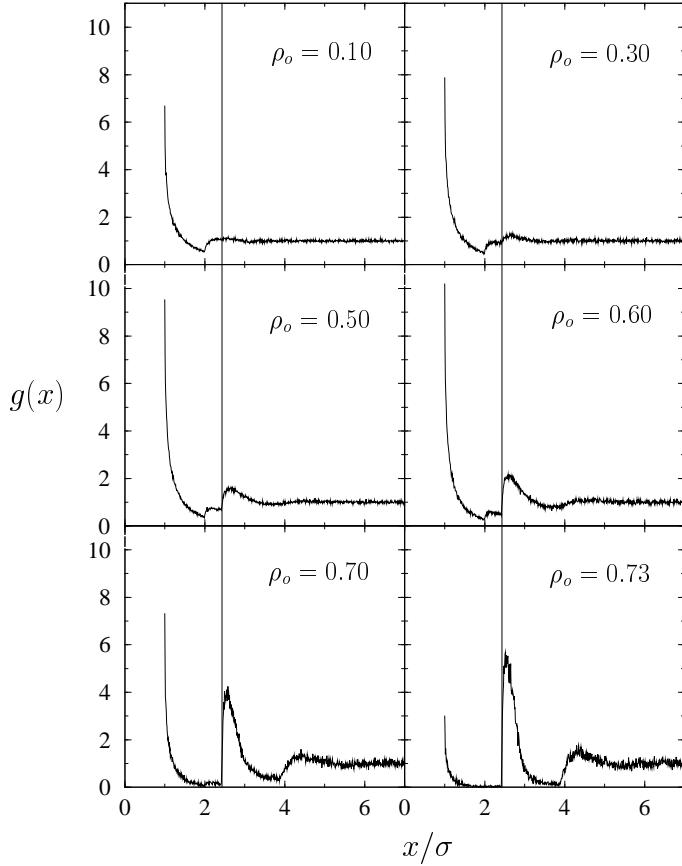


Fig. 2 – Particle-particle correlation function for fixed $r = 0.70$ and different initial coverages ρ_0 .

one obstacle, such that the distance between the centers of the particles in a pair is $x = \sigma + \sigma_0$ or $x/\sigma = 1 + 1/r \simeq 2.429$. This value has been marked in Fig. 1 by means of a straight vertical line. For even larger values of the initial concentration, $\rho_0 \geq 0.70$, a third peak in the correlations is also observed.

In summary, we have studied the kinetics of adsorption onto a line under the conditions for which the density of gaps among particles is not scale invariant. The analysis of the process, governed by the RSA rules, has revealed the existence of new and rich phenomenology beyond the scaling regime, including: substantial increase in the jamming limit, which depends on the density of inhomogeneities introduced; the appearance of new correlations among the particles; and also the existence of a critical density of impurities, dividing regimes of soft and complete violation of the scaling symmetry. To this purpose, we have proposed and solved analytically a continuous 1d model in which particles adsorb, following the RSA rules, onto a surface in which spherical particles of different size have been previously scattered. When particularized to the case in which the imposed length scale is smaller than the size of the particles, our model reproduces the results obtained from a previous model considering the adsorption on a lattice in the presence of point-like impurities. Our results may offer new perspectives on what concerns modelization of the adsorption phenomena in more complex surfaces, as the ones having a certain roughness or an intrinsic structure manifested through

the existence of a characteristic correlation length. In those surfaces, found in situations of practical interest, the property of scale-invariance, inherent to standard adsorption models, is no longer satisfied.

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